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LIFETIME OF SINGLET OXYGEN IN AQUEOUS HYDROGEN PEROXIDE (BHP)

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Final Report

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Singlet delta oxygen lifetime in deuterated basic hydrogen peroxide was measured. The contributing bimolecular rate constants k_{OO^-} and $k_{D_2O_2}$ were measured as a function of temperature. The measured lifetime of 20 μs compared favorably to the lifetime of 24 μs arrived at by using contributing bimolecular rates.

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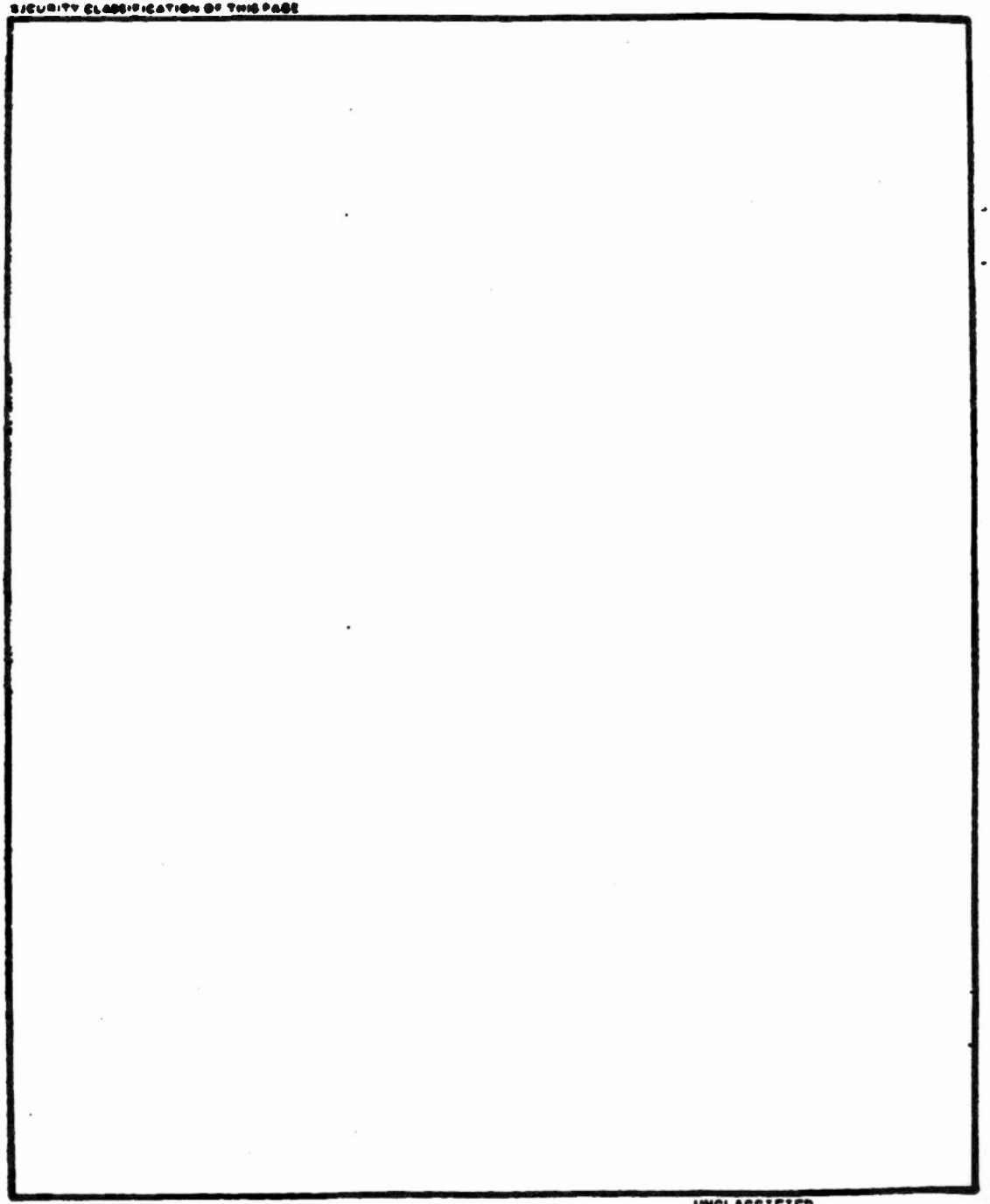


SUMMARY

The lifetime (τ_Δ) of singlet molecular oxygen $O_2(^1\Delta_g)$ in aqueous solution is little affected by the presence of the species OH^-, H_2O_2 or OD^- and D_2O_2, compared with its lifetime in either H_2O or D_2O, respectively.

The bimolecular quenching rate constants for the quenching of $O_2(^1\Delta_g)$ by OD^- and D_2O_2 have been determined as 5.5×10^3 $M^{-1}s^{-1}$ and 8.8×10^2 $M^{-1}s^{-1}$, respectively. A direct measurement of the bimolecular quenching rate constants for OH^- and H_2O_2 was not possible due to instrumental limitations.

Fully deuterated basic hydrogen peroxide (BHP) at -20°C yielded a lifetime of 20 μs for $O_2(^1\Delta_g)$ by direct measurement, but a reliable direct measurement of τ_Δ under BHP conditions was not possible. However, using reasonable assumptions, we estimate τ_Δ in BHP at -20°C to be 1.8 μs.

The temperature dependencies of all the rate parameters have been measured, yielding activation energies close to 6 kJ mol^{-1}.

The current development of a novel singlet oxygen detector, which should have improved bandwidth, will be used to re-examine τ_Δ in BHP by direct measurement.

PREFACE

The Rotocoil singlet oxygen generator produces $O_2(^1\Delta_g)$ chemically by reacting chlorine gas with basic hydrogen peroxide solution (BHP).

Although the lifetime of $O_2(^1\Delta_g)$ has been measured in many solvent systems and has been found to be very solvent-dependent, it has never been determined under BHP conditions. In a solution of BHP such as that used in the Rotocoil generator, which is water with high concentrations of hydroxide ion (OH^-) and hydrogen peroxide (H_2O_2), the possibility of additional deactivation modes are introduced.

These deactivation processes under conditions of high concentrations of hydroxide and hydrogen peroxide have been investigated, as well as the effects of temperature on $O_2(^1\Delta_g)$ deactivation.

CONTENTS

1.0 INTRODUCTION

The lifetime of $O_2(^1\Delta_g)$ in solution is solvent dependent (Refs. 1-4) and may vary by up to a factor of several hundred in common organic solvents. The lifetime (τ_Δ) of the $^1\Delta_g$ state also displays a solvent deuterium isotope effect (Ref. 1). In pure H_2O, $\tau_\Delta = 4$ μs; and in pure D_2O, $\tau_\Delta = 62$ μs. The introduction of species such as OH^- and H_2O_2 into the solvent system may introduce additional deactivation modes for the $^1\Delta_g$ state (eqns. 6 and 7). Deactivation of the electronic excitation energy of $O_2(^1\Delta_g)$ is thought to occur via energy transfer to solvent vibrational modes (Ref. 1).

The lifetimes of $O_2(^1\Delta_g)$ in this report were determined by time-resolved studies of the singlet oxygen luminescence at 1270 nm ($^1\Delta_g$ v=0 to $^3\Sigma_g$ v=0 transition). Singlet oxygen was produced in solution by flash excitation of a sensitizing dye which undergoes energy transfer to oxygen from its triplet state. The overall kinetic scheme for production and decay is as follows:

$$S + h\upsilon = {}^1S^* \quad (1)$$

$${}^1S^* = {}^3S^* \quad (2)$$

$${}^3S^* + O_2(^3\Sigma_g) = S + O_2(^1\Delta_g) \quad (3)$$

$$O_2(^1\Delta_g) = O_2(^3\Sigma_g) \quad (4)$$

$$O_2(^1\Delta_g) = O_2(^3\Sigma_g) + h\upsilon \quad (5)$$

$$O_2(^1\Delta_g) + H_2O_2 = O_2(^3\Sigma_g) + H_2O_2 \quad (6)$$

$$O_2(^1\Delta_g) + OH^- = O_2(^3\Sigma_g) + OH^- \quad (7)$$

The luminescence of singlet oxygen at 1270 nm was detected using a germanium-photodiode-based system. The decay of the $O_2(^1\Delta_g)$ luminescence signal follows first-order kinetics. A representative decay trace is shown in Figure 1. A fast emission spike, thought to be due to sensitizer emission in the near infrared region, is seen at the beginning of the decay signal; however, after the decay of the spike, the kinetics are first-order. Semilogarithmic plots of the data are linear, Figure 2, confirming the first-order kinetics. The slope of the semilogarithmic plot yields the lifetime of singlet oxygen in that medium.

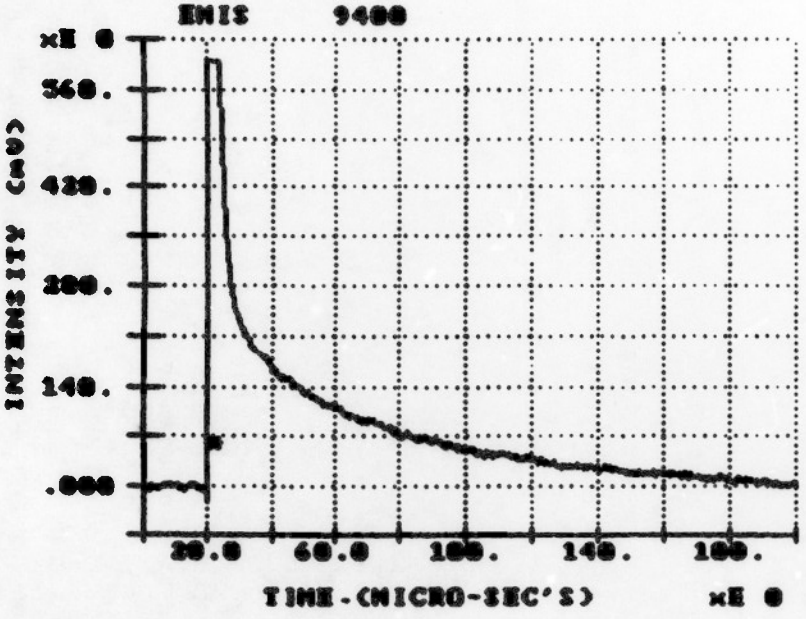


Figure 1. Luminescence decay of singlet oxygen at 1270 nm.

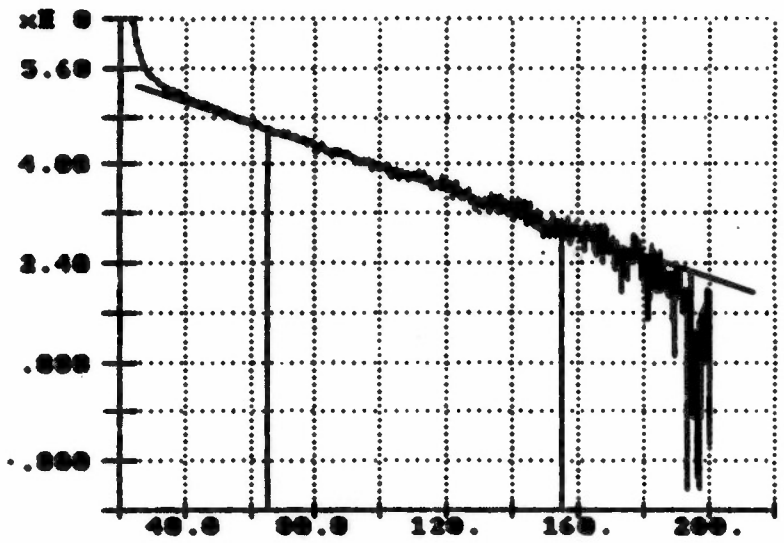


Figure 2. Semilogarithmic plot of figure 1.

However, the fast spike causes severe problems to measurements of systems having τ_Δ of a few microseconds. Luminescence yields from $O_2(^1\Delta_g)$ are relatively weak compared to the intense fast emission. The latter has an exponential tail which, when τ_Δ are circa a few microseconds, merges with the singlet oxygen luminescence signal and becomes indistinguishable therefrom. For this reason we have been unable to obtain reliable direct data for the value of τ_Δ in BHP (protiated), see below.

2.0 EXPERIMENTAL

2.1 APPARATUS

The excitation source was a Quantel YG571C Q-switched Nd:YAG laser, producing circa 10 ns pulses with up to 1084 mJ per pulse at 1064 nm. The second (532 nm) and third (355 nm) harmonics were generated and separated from the fundamental by two successive dichroic mirrors and a heat-absorbing filter.

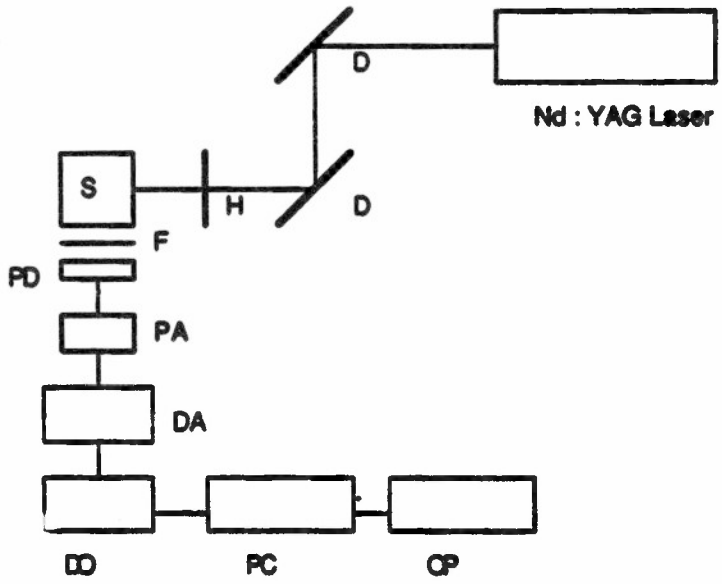
The luminescence from the irradiated solutions was detected using a germanium photodiode operating with a 6 volt reverse bias. The signal was fed into a Judson 100 preamplifier providing 55 dB of gain, followed by a differential amplifier operating at unit gain, to provide impedance matching with the input of the LeCroy 9400 digital oscilloscope. The LeCroy was on-line to an IBM PC/AT clone microcomputer. For all lifetime measurements, between 10 and 20 individual decay curves were taken and averaged in the computer. The entrance to the diode housing was covered with a 5-mm-thick piece of antireflection coated silicon which has a cut-on at 1050 nm. A 10x10 mm quartz fluorescence cell was placed in contact with the filter. The luminescence was monitored at 90^0 to the incident laser beam. The fluorescence cell was housed in an aluminium holder which could be heated or cooled from -30^oC to $+50^oC$ by a circulating 1:1 water/ethylene glycol solution from a thermostatically controlled circulator. Temperature measurements were made using a Cole-Palmer 85671 bench indicator connected to a T-type thermocouple. This experimental setup is shown schematically in Figure 3.

2.2 SAMPLE PREPARATION

In aqueous solution the following sensitizers were used; rose bengal (RB), pyrene tetrasulfonic acid tetrasodium salt (PTSA) and meso-tetra (4-sulfonato-phenyl) porphine tetrasodium salt (TPPS). The optical densities at 532 nm and 355 nm were 0.6/cm. All solutions were oxygen saturated prior to irradiation. Saturation of the solutions with argon gas completely removed the $O_2(^1\Delta_g)$ luminescence.

The solvents used were, D_2O (99.8% atom), and deionized water purified through a nano-pure filter system, 30 wt% D_2O_2 in D_2O and 30 wt% H_2O_2.

Reagent grade potassium hydroxide and sodium deuteroxide (99.8% atom) were used as quenchers.



D - DICHROIC MIRROR
H - HEAT FILTER
S - SAMPLE CELL
F - SILICON FILTER
PA - PREAMPLIFIER
DA - DIFFERENTIAL AMPLIFIER
DO - DIGITAL OSCILLOSCOPE
PC - COMPUTER
OP - OUTPUT
PD - PHOTODIODE

Figure 3. Schematic of singlet oxygen luminescence detection system.

3.0 RESULTS

3.1 DIRECT MEASUREMENTS OF THE SINGLET OXYGEN LIFETIME

3.1.1 Perprotio BHP

For the reasons of luminescence impurity outlined above, a solution of BHP (25% H_2O_2 and 25% KOH in H_2O at -20°C) containing PTSA as sensitizer did not yield a reliable direct measurement of τ_Δ. It is possible to state that the value is not greater than 7 μs. The indirect approach is detailed in section 3.2.

3.1.2 Perdeutero BHP

Singlet oxygen deactivation by solvent shows a dramatic isotope effect. The enhancement achieved by fully replacing all H atoms by their deuterium counterpart are often in the range of 10-20 times the undeuteriated value. We prepared a sample of perdeutero BHP (BHP^*) containing 25% NaOD and 25% D_2O_2 in D_2O at -20°C with PTSA as sensitizer. Laser pulse excitation produced an infrared (IR) signal from singlet oxygen that was kinetically distinguishable from the decay of the rapid spike (Figure 4). From this we obtained $\tau_\Delta(BHP^*) = 20$ μs. This experiment could be performed only at sub-zero temperatures, as the BHP^* decomposed above -10°C.

To support this direct measurement and to provide data to allow an evaluation of $\tau_\Delta(BHP)$, we carried out indirect measurements as detailed below.

3.2 INDIRECT EVALUATION

The strategy of this approach is to evaluate bimolecular rate constants (where possible) for the deactivation processes:

$$O_2(^1\Delta_g) + OH^- = O_2(^3\Sigma_g) + OH^- \quad (8)$$

$$O_2(^1\Delta_g) + OD^- = O_2(^3\Sigma_g) + OD^- \quad (9)$$

$$O_2(^1\Delta_g) + H_2O_2 = O_2(^3\Sigma_g) + H_2O_2 \quad (10)$$

$$O_2(^1\Delta_g) + D_2O_2 = O_2(^3\Sigma_g) + D_2O_2 \quad (11)$$

and the temperature dependences of the these processes. In this way we can expect to evaluate τ_Δ from the relationship:

$$\tau_\Delta(BHP)^{-1} = k_d(BHP) = k_O + k_{OH^-}[OH^-] + k_{H2O2}[H_2O_2] \quad (12)$$

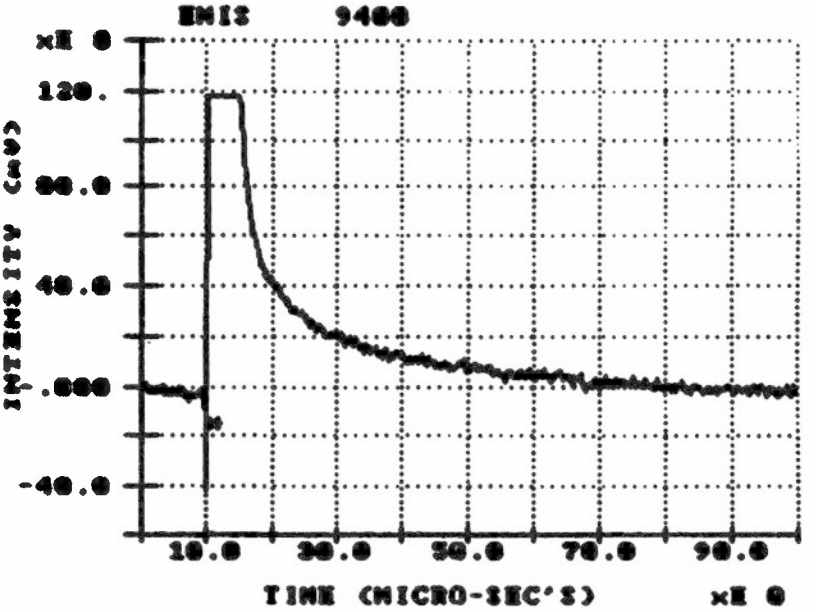


Figure 4. Luminescence decay of singlet oxygen in deuterated BHP.

where $k_O = (\tau_\Delta)^{-1}$ is the deactivation rate constant in neat water. These k_O values for both H_2O and D_2O are known from the literature (Ref. 4).

3.2.1 Quenching of $O_2(^1\Delta_g)$ by D_2O_2

D_2O_2 was shown to quench $O_2(^1\Delta_g)$ only weakly. Figure 5 depicts a plot of the decay rate (s^{-1}) of the IR luminescence as a function of D_2O_2 concentration in D_2O over the range 0-10 M at 20°C. The plot is linear as expected for a first-order dependence on concentration. The bimolecular rate constant (k_{D2O2}) evaluated from the slope of Figure 5 is 8.8×10^2 $M^{-1}s^{-1}$.

3.2.2 Quenching of $O_2(^1\Delta_g)$ by OD^-

An analogous series of experiments to those described in 3.2.1 were carried out at 20°C but replacing D_2O_2 by NaOD. The decay of $O_2(^1\Delta_g)$ luminescence was exponential and Figure 6 shows a linear relationship between the measured decay constant and OD^- concentration. From this $k_{OD^-} = 5.5 \times 10^3$ $M^{-1}s^{-1}$.

3.2.3 Quenching by H_2O_2 and OH^-

The lifetime of singlet oxygen in H_2O is 4 μs, which is at the low end of reliable measurements because of sensitizer-derived emission spiiiing over in the iR measuring region. Thus we were unable to measure any decreases in this value caused by quenching additives such as H_2O_2 and OH^-.

3.3 TEMPERATURE DEPENDENCE OF τ_Δ

3.3.1 IN D_2O

Over the temperature range 278-323 K, the value of $\tau_\Delta(D_2O)$ varied from 71 μs to 48 μs with a value of 61 μs at room temperature (20°C). An Arrhenius plot of the data using a variety of sensitizers (Figure 7) showed linear behavior from which the relationship (equation 13) is obtained.

$$k_O(T) = 1.88 \times 10^5 \exp(-714/T)\ s^{-1} \qquad (13)$$

3.3.2 In 25% D_2O_2 in D_2O

For a 25% D_2O_2 solution in D_2O measured over a range of temperature from 258-283 K, an Arrhenius plot of the first-order deactivation rate parameter (in s^{-1}) yielded

$$k_d(D_2O_2/D_2O) = 3.57 \times 10^6 \exp(-1408/T)\ s^{-1} \qquad (14)$$

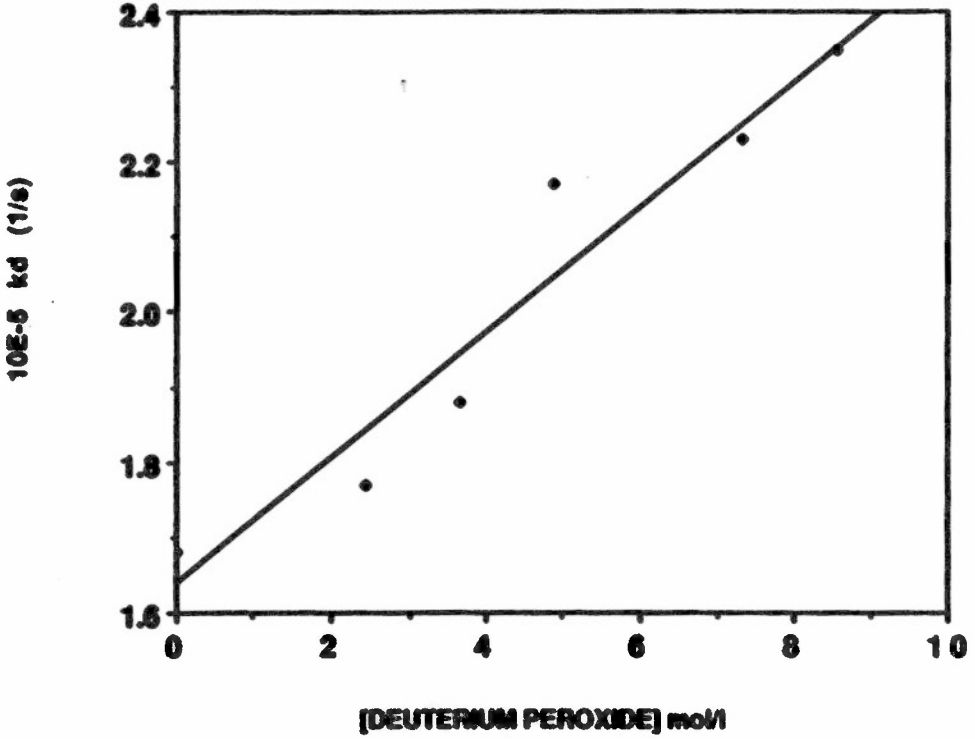


Figure 5. kd vs concentration of deuterium peroxide.

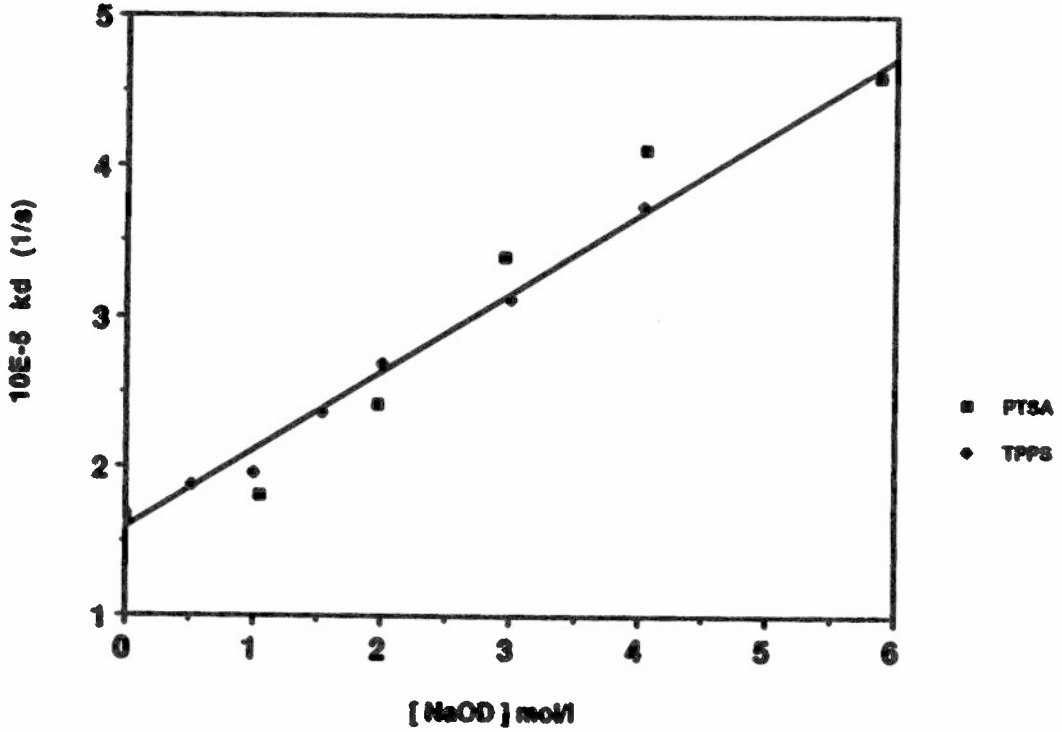


Figure 6. kd vs concentration NaOD.

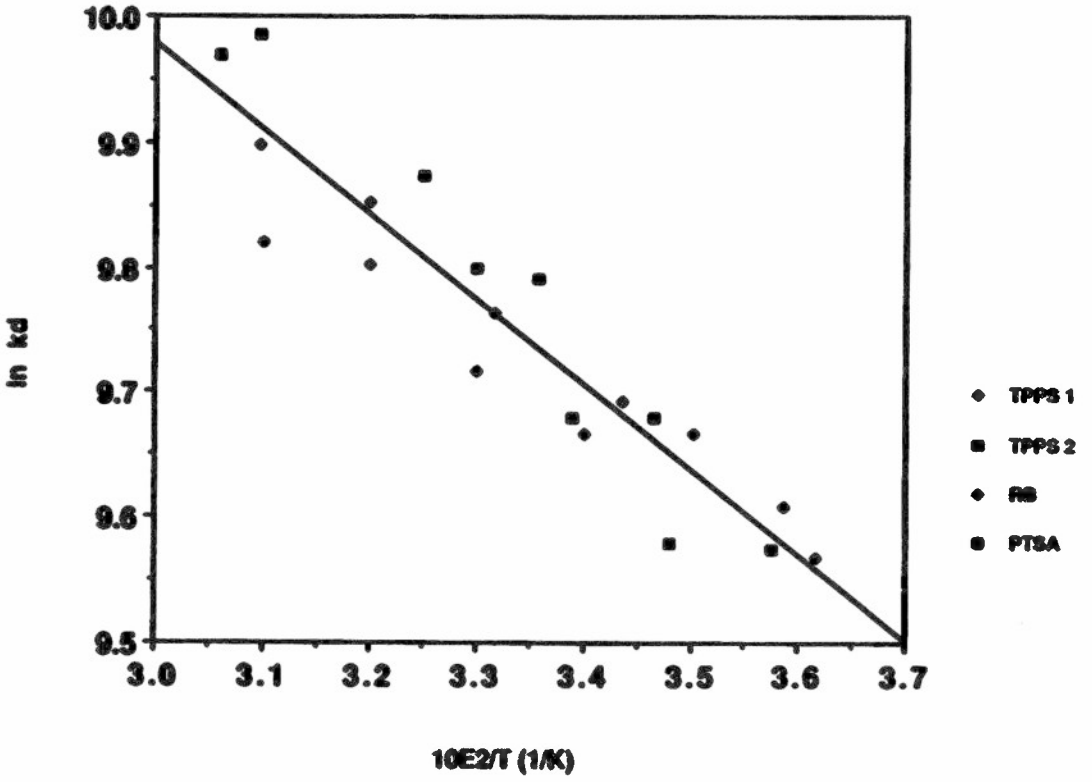


Figure 7. Arrhenius plot of temperature dependence of singlet oxygen lifetime.

3.3.3 3 Molar OD^- in D_2O

An Arrhenius plot of the first-order decay of $O_2(^1\Delta_g)$ in an alkaline (OD^-) solution in D_2O yielded

$$k_d(OD^-/D_2O) = 3.8 \times 10^5 \exp(-660/T)\ s^{-1} \qquad (15)$$

4.0 DISCUSSION

4.1 COMPARISON OF DIRECT AND INDIRECT EVALUATIONS

4.1.1 Perdeutero-BHP

As indicated before, the deactivation rate constant of a mixture of BHP components in the general case is given by:

$$k_T = k_O + k_P[\text{peroxide}] + k_B[\text{base}] \qquad (16)$$

where k_O is the first-order constant for the deactivation in the neat solvent, and k_P and k_B are bimolecular rate constants for deactivation by peroxide and base species respectively. All rate parameters in equation (16) are temperature dependent, but only very weakly so (E_a values are near 6 kJ mol^{-1}). For deuterated materials, we have determined values of k_O, k_P and k_B at 20°C. These are 1.7×10^4 s^{-1}, 8.8×10^2 $M^{-1}s^{-1}$, and 5.5×10^3 $M^{-1}s^{-1}$, respectively.

The BHP and BHP° systems we made contained 25% by weight of peroxide and base components. This yields $[OD^-] = 4.8$ M and $[D_2O_2] = 6.6$ M. From these rate constants and concentration values we can evaluate k_T (BHP°) from

$$k_T = 1.7 \times 10^4 + (8.8 \times 10^2 \times 6.6) + (5.5 \times 10^3 \times 4.8) = 4.9 \times 10^4 \ s^{-1} \qquad (17)$$

and, since $\tau_\Delta(\text{BHP}) = k_T(\text{BHP}^\circ)^{-1}$, $\tau_\Delta(\text{BHP}^\circ) = 20.4$ μs at 20°C by indirect evaluation, which compares to 20 μs by direct measurement at -20°C. Thus, from $k_O = 1.88 \times 10^5 \exp(-714/T)$ s^{-1}, we find $k_O(-20^\circ C) = 1.13 \times 10^4$ s^{-1}.

From $k_d(T) = 3.8 \times 10^5 \exp(-660/T)$ s^{-1} for 3 M OD^-/ D_2O, we find $k_B[OD^-]$ $(-20^\circ C) = 2.7 \times 10^4$ s^{-1} at 4.8 M OD^-.

From $k_d(T) = 3.57 \times 10^6 \exp(-1408/T)$ s^{-1} for 6.6 M D_2O_2/D_2O, we find $= k_P[D_2O_2] = 3.0 \times 10^3$ s^{-1} at 6.6 M D_2O_2.

Therefore $\Sigma k = 1.13 \times 10^4 + 2.7 \times 10^4 + 3.0 \times 10^3 = 4.1 \times 10^4$ s^{-1} and $\tau_\Delta = \Sigma k^{-1} = 24.3$ μs.

This value is close enough to the direct measurement of 20 μs at -20°C for τ_Δ in BHP° to give us confidence in the procedure. One useful fact to

note is that the contribution of D_2O_2 to the total decay is only circa 7% and is therefore relatively insignificant.

4.1.2 Estimation of Singlet Oxygen Lifetime in BHP

Experimental problems have prevented the direct measurement of τ_Δ in BHP and the values of k_{OH^-} and k_{H2O2} in order to make the indirect evaluation. However, an estimate can be made as follows.

In the equation for overall decay:

$$k_T = k_O + k_B[Base] + k_P[Peroxide]$$

We have shown in the previous section that the $k_P[Peroxide]$ factor is small enough to be ignored. Then

$$k_T = k_O + k_B[Base] \qquad (18)$$

We know k_O for H_2O at 20°C from the literature, and by assuming the same exponential temperature parameter (714 K) as for D_2O, we can equate the ratios of the pre-exponential factors (A values) to that of the rate constant at 20°C.

Thus: $$A_O(H) = A_O(D) \cdot k_O(H)/k_O(D) \qquad (19)$$

$$= 1.88\times10^5 \times \frac{2.5\times10^5}{1.7\times10^4} = 2.8\times10^6\ s^{-1}$$

From this we write down the Arrhenius expression for $k_O(H_2O)$ as

$$k_O(H_2O) = 2.8\times10^6 \exp(-714/T)\ s^{-1} \qquad (20)$$

and, at -20°C (253 K), this will contribute $1.7\times10^5\ s^{-1}$ to the total decay (k_T).

We cannot use the same expression to estimate $k(OH^-)$ since we do not have data for OH^-/H_2O solution at 20°C. However, we can make an argument based upon literature values for relative contributions (Δ_{OX}) to the singlet oxygen deactivation by OH and OD oscillators in alkanols (Ref. 5). Thus, $\Delta_{OH} = 2290$ and $\Delta_{OD} = 165$; and if we assume the ratio (H/D = 14) (Ref. 5) applies equally well to OH^- and OD^- species, then we can convert $k_{OD^-}[OD^-] = 2.7\times10^4\ s^{-1}$ at -20°C into $k_{OH^-}[OH^-] = 3.8\times10^5\ s^{-1}$.

In equation (18), therefore,

$$k_T = 1.7\times10^5 + 3.8\times10^5 = 5.5\times10^5\ s^{-1} \text{ at } -20°C$$

or $\tau_\Delta(BHP) = 1.8\ \mu s$ in BHP at -20°C.

5.0 CONCLUSIONS

These experiments have led to the following conclusions:

(1) Fully deuterated BHP at -20°C supports a lifetime of 20 μs for $O_2(^1\Delta_g)$ by direct measurement. This compares to 60 μs at room temperature for D_2O alone.

(2) The contributing bimolecular rate constants k_{OD^-} and k_{D2O2} have been determined and their temperature dependence measured. These data have allowed an indirect estimation of τ_Δ for deutero-BHP of 24 μs, very close to the directly measured value.

(3) Instrumental limitation prevented direct measurement of τ_Δ in BHP at -20°C and of k_{OH^-} and k_{H2O2}. However, using reasonable assumptions, we estimate τ_Δ in BHP at -20°C to be 1.8 μs.

(4) After completion of this program, a novel singlet oxygen detector has been developed which should have improved bandwidth. If so, it will be used to re-examine BHP (direct).

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